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Effect of nanostructure on corrosion and corrosion resistance of materials

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Abstract

Significant progress has been made in various aspects of synthesis of nanostructured materials. The nanostructured materials, with their grain sizes or phase dimensions in the nanometer size regime, are produced by a wide variety of synthesis and processing methods. Nanomaterials are characterized by their small grain sizes (1-100 nm) and high volume fraction of grain boundaries, which often gives rise to unique physical, chemical and mechanical properties compared with those of their cast counterparts. These properties have been found particularly useful in corrosion protection applications. The application of nanotechnology in the field of corrosion prevention of metals attracts the attention of researchers. nanostructures promote selective oxidation, forming a protective oxide scale with superior adhesion to the substrate. A polymer nanocomposite coating can effectively combine the benefits of organic polymers, such as elasticity and water resistance to that of advanced inorganic materials, such as hardness and permeability. The nanostructured silica coating showed comparable or better performance than hexavalent chrome passivation. Mild steel is protected by an eco-friendly nanostructured conducting polymer/oil polyurethane composites

Keywords

Nanomaterials; Properties of nanomaterials; Nanostructure and corrosion; Corrosion prevention.

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INTRODUCTION

Nanostructured materials (1–100 nm) are known for their outstanding mechanical and physical properties due to their extremely fine grain size and high grain boundary volume fraction^[1]. They are important due to their unique properties that may lead to new and exciting applications^[2]. The application of nanotechnology in the field of corrosion prevention of metals attracts the attention of researchers. Many of these applications require good understanding of the corrosion behavior of the materials as a function of microstructure. Significant progress has been made in various aspects of synthesis of nano-scale materials. In addition, nanostructures promote selective oxidation, forming a protective oxide scale with superior adhesion to the substrate. A polymer nanocomposite

coating can effectively combine the benefits of organic polymers, such as elasticity and water resistance to that of advanced inorganic materials, such as hardness and permeability^[3]. The nanostructured silica coating showed comparable or better performance than hexavalent chrome passivation^[4]. Such behavior of nanostructured materials, which relates to corrosion resistance, relies on materials microstructure. As known, most properties of solids depend on the materials microstructure. The microstructure includes a number of parameters, which are the chemical composition, the arrangement of the atoms (the atomic structure) and the size of a solid in one, two or three dimensions^[5]. If one or several of these parameters are changed, the properties of a solid vary. The most well-known example of the correlation between the atomic structure and the properties of a bulk material is prob-

ably the spectacular variation in the hardness of carbon when it transforms from diamond to graphite. Comparable variations have been noted if the atomic structure of a solid deviates far from equilibrium or if its size is reduced to a few interatomic spacing in one, two or three dimensions. An example of the latter case is the change in color of CdS crystals if their size is reduced to a few nanometers^[6]. The focus is shifting from synthesis to manufacture of useful structures and coatings having greater wear and corrosion resistance.

DEFINITION OF CORROSION

Corrosion could be defined as “the chemical or electrochemical reaction between a material and its environment that produces deterioration of the material or of its properties”. Also, corrosion is considered as including combined forms of attack in which the simultaneous occurrence of corrosion by chemical or electrochemical attack^[7-9]. The basic corrosion theory is that the corrosion is an electrochemical reaction composed of two half cell reactions, an anodic reaction and a cathodic reaction. The anodic reaction releases electrons (equation 1), while the cathodic reaction consumes electrons (equations: 2-5). Each half-cell reaction has an electrical potential, known as the half-cell electrode potential. The anodic reaction potential, E_a , plus the cathodic reaction potential, E_c , adds up to E , the cell potential. If the overall cell potential is positive, the reaction will proceed spontaneously. The corrosion reactions can be represented as follows:

Anodic reaction



Where M stands for a metal and n stands for the number of electrons that an atom of the metal will easily release, i.e. for iron and steel:

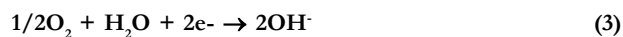


Cathodic reactions

➤ Oxygen reduction in acidic solution



➤ Oxygen reduction in neutral or basic solution



➤ Hydrogen evolution from acidic solution



➤ Hydrogen evolution from neutral water



The chemical attack or dry corrosion occurs under dry conditions, such as high temperatures in gaseous environments, molten salts and liquid metals. Dry corrosion process is a direct reaction between a metal and the corrosive environment. Dry corrosion is of great importance in a number of petroleum refining processes. It includes the attack of hydrogen sulfide and other sulfur compounds on steel and various alloys at elevated temperatures. Solutions to this type of corrosion generally depend on metallurgical approaches, e.g. variations in composition, heat treatment of the selected metal or alloy. In fact, high temperature corrosion of metals and alloys always involves oxidation process. For example, a metal reacts with oxygen at high temperature by initial adsorption of oxygen, chemical reaction to form the surface oxide, oxide nucleation and lateral growth into a continuous film. Such film may protect the underlying metal^[10]. One of the well known oxidation is the iron oxidation in oxygen (as pure metal or in carbon steel alloys) at high temperature^[11].

Wet corrosion is an electrochemical process; in practice it is limited to nearly 232 °C as an upper temperature. The electrochemical corrosion results from reaction between a metal surface and an ion-conducting environment. This process can occur if the metal contact with an electrolyte for transport of electric current. Most cases of electrochemical corrosion proceed in aqueous media such as natural water, atmospheric moisture, rain, and wet soil. Also, other environments e.g. acids, petroleum products, cooling water, chemical solutions,...etc. For example, water is presented in refinery by different sources, such as the crude itself, through injection of water or steam to aid in the steam distillation of various petroleum fractions, water washing or aqueous solution contacting various intermediate and product streams in refining and petrochemical processes^[7].

Corrosion cells

Corrosion cells are created on metal surfaces in contact with an electrolyte because of energy differences between the metal and the electrolyte. Different area on the metal surface could also have different potentials with respect to the electrolyte^[12,13]. These variations could be due to i) metallurgical factors, i.e., differences in their composition, microstructure, fabrication, and field installations, and ii) environmental factors. Carbon and low alloy steels are the most widely used material in different industries in corrosive environments and the metallurgical factors have great influence on the corrosion process^[14,15].

Enhancing corrosion resistance

In order to enhance the corrosion resistance of metals, many ways have been developed, for example, adding passive alloy element, applying inhibitors, and putting protective coating and so on. Among these various methods, changing micro-structure of materials by using new micro-structures such as single crystalline (SC), nanocrystalline (NC) or microcrystalline (MC) and amorphous to replace the traditional cast alloy, will bring surprised results to promote the corrosion resistance of metals/alloys^[16-19]. NC materials are characterized by their small grain sizes (1-100 nm) and high volume fraction of grain boundaries, which often gives rise to unique physical, chemical and mechanical properties compared with those of their cast counterparts^[16,19]. These properties have been found particularly useful in corrosion protection applications.

CORROSION BEHAVIOUR OF NANOSTRUCTURED ALLOYS

Electrodeposition is a versatile technique for producing nanostructured materials. It is a technologically and economically viable production route to metals, alloys and metal matrix composites, both in bulk form and as coatings. Properties of nano-structured electrodeposits such as hardness, wear resistance and electrical resistivity are strongly grain size dependent. Corrosion behaviour of nanostructured-alloys has been assessed by several techniques in various environments^[20-23]. Thorpe et al.^[20] reported an enhanced corrosion resistance of nanostructured- Fe₃₂-Ni₃₆-Cr₁₄-P₁₂-B₆ than that of its amorphous counterpart. The authors attributed this improved corrosion resistance to the observed greater Cr-enrichment of the electrochemical surface film via rapid interphase boundary diffusion. Bragagnolo et al.^[21] reported improved corrosion resistance with nanostructured-Fe₇₂Si₁₀B₁₅Cr₃ metallic glass wires. In their study, the beneficial effects of nanostructured processing for corrosion resistance were not evident with a non-passivating alloy composition. Zeiger et al.^[22] reported an enhanced corrosion resistance of nanostructured-Fe-8 wt% Al in Na₂SO₄ solution. The study showed that defect density (density of grain boundaries) promotes metal dissolution. As the diffusion of aluminum is fast enough in the grain boundaries, it is possible that the oxide film on nanostructured and crystalline-FeAl₈ alloy provides better protection than on the same polycrystalline alloy. The passive film formation of nanostructured-FeAl₈ is distinctly eased in

the pH range (weakly acidic to weakly basic) where Al forms stable passive film. The newly developed Ti₆₀Cu₁₄Ni₁₂Sn₄Nb₁₀ nanostructured dendrite composite exhibits a particular microstructure that confers outstanding mechanical properties and improves corrosion resistance^[24]. It has been reported that the presence of a ductile second phase can significantly improve the mechanical properties of nanocrystalline alloys. The usual low ductility of homogeneous nanocrystalline alloys is greatly enhanced in a promising, newly developed Ti-base bulk alloy with a dendritic phase dispersed in a nanostructured matrix, backscattered electron image shows the structure as in Figure 1. Polarization tests of Ti₆₀Cu₁₄Ni₁₂Sn₄Nb₁₀ copper mould cast specimens indicate good corrosion resistance in acidic media (0.5N H₂SO₄), medium resistance in alkaline (0.5N NaOH) but the alloy undergoes pitting in chloride media (1, 0.1 and 0.01N NaCl) Figure 2. The behaviour of the alloy in H₂SO₄ is similar as the typical behaviour of pure titanium and titanium alloys^[25], exhibiting a wide anodic passive region between 90mV and 1.5V (SCE), approximately, and passive current densities in the order of 10⁻³ mA due to the formation of highly protective surface films. In NaOH electrolyte the voltage range of passivation is shorter than in H₂SO₄, finishing when the current increased to 470mV (SCE), approximately. Similar passive currents densities as in H₂SO₄ are attained. In chloride media, the passivation during anodic polarization is interrupted by a sharp increase in current density indicating the initiation of pitting corrosion by a sudden passive film breakdown followed by an excessive pit growth and the subsequent dissolution of the surface of the alloy. pitting potentials were shifted to more negative values when concentration of NaCl increased. This behaviour differs from general findings on polycrystalline pure titanium and dilute titanium alloys, in which pitting corrosion and localized attack are not observed in marine environments^[26].

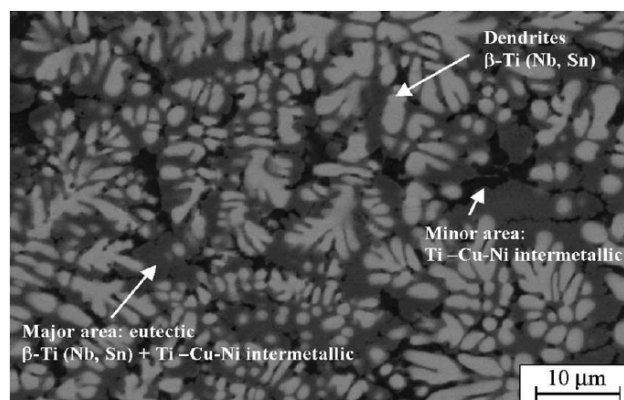


Figure 1 : Backscattered electron image of the as-cast Ti₆₀Cu₁₄Ni₁₂Sn₄Nb₁₀ alloy^[24]

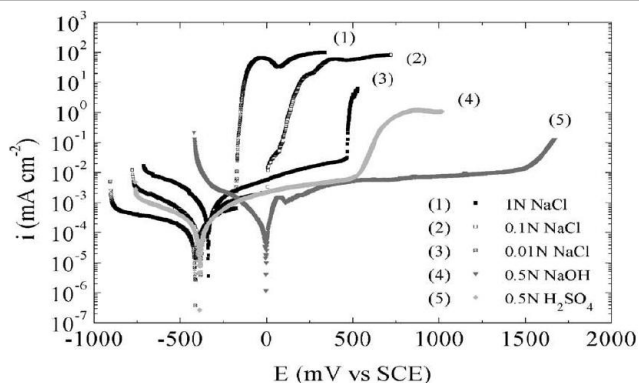


Figure 2 : Potential vs. current density curves of the Ti60Cu14Ni12Sn4Nb10 alloy in 1, 0.1 and 0.01N NaCl, 0.5N NaOH and 0.5N H₂SO₄ electrolytes by potentiodynamic polarization measurements^[24].

NANOSTRUCTURE AND CORROSION RESISTANCE

Mild steel corrosion resistance

Mild steel, for example, widely used as a structural material in engineering applications is prone to corrosion and wear and consequently has limited service life unless effective measures are taken to improve its corrosion and wear resistance properties^[27-31]. Since mild steel is inexpensive and widely used, new and low-cost corrosion protection treatment are always sought. Passive protection is normally provided by a barrier film precluding contact between corrosive environment with the metallic surface. However, weakness of the barrier layer could trigger corrosion. The use of inhibitive species that can decrease corrosion intensity constitutes active corrosion protection. The use of both strategies jointly could adequately protect the metallic substrate. The conversion coatings such as chromating and phosphating treatments have historically played important role in different industries by providing corrosion protection to both ferrous and non-ferrous metals. Also in many cases the anticorrosive property of zinc phosphate treatment is insufficient for outdoor exposure, while electroplated Ni and Cr, even though effective are relatively expensive and Cr(VI) is environmentally unacceptable^[32]. As an alternative, siloxane based sol-gel coatings have been suggested as passive corrosion protection due to the ability to form dense Si-O-Si network adhering to substrate through Me-O-Si bonds, both of which confer good corrosion impeding properties^[33-39]. Adhesion of the coating may be improved further by adding specific organic functional groups like epoxy in siloxane molecule. Silica network can also be reinforced by clusters of metal oxides produced during sol-gel synthesis from the respective metal alkoxides^[40,41].

Additionally, sol-gel coatings do not need high process temperature and vacuum conditions crucial in the case of many of thin layer coating techniques^[42-45]. Furthermore, sol-gel is relatively simple, low-cost and applicable to materials having complex geometry and also they are considered to have low negative environmental impact. Nevertheless, defects or pores in the sol-gel coating lets in the corrosive species and initiates the corrosion processes^[46] which gives rise to the need for additional active corrosion protection. Incorporation of inhibitive species into inorganic fillers^[47,48] encapsulation of organic inhibitors through plasma polymerization^[45] or layer-by-layer assembly of polyelectrolyte^[46,47] enhance corrosion resistance. Many kinds of inhibitors could be used to protect various metallic materials^[48-57]; however, very often this negatively influences the stability of the sol-gel matrix^[58,59]. Acetylenic alcohols are considered excellent inhibitors of corrosion^[60].

The defects of sol-gel protection can be treated by using nanostructure sol-gel impregnated with propargyl alcohol^[61]. Uncoated (MS) as well as three differently prepared surface samples' polarization curves from mild steel specimens double coated by sol-gel layers and immersed in 0.5M NaCl for 20min are shown in Figure 3. Both strongly anodic and moderate cathodic reactions of mild steel samples are affected but etched samples show remarkably lower corrosion currents as compared with the mechanically polished or electropolished samples.

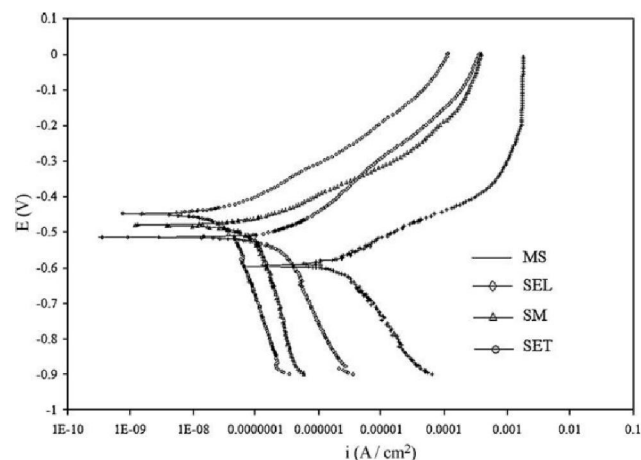


Figure 3 : Polarization plots obtained in 0.5M NaCl solution for bare mild steel electrode (MS), sol-gel coating on mechanical polished surface (SM), on electropolished surface (SEL), and on etched surface (SET)^[61].

Owing to the stringent environmental regulations on the usage of toxic heavy metals in the formulation of corrosion protective coatings, anticorrosive primers and coatings based on conducting polymers are gain-

ing momentum^[62,63]. The recent advancements in nanotechnology have hastened the development of high performance nanostructured coatings having a broad spectrum of anticorrosive activity under a wider range of hostile environments. Inhibitor coatings based on conducting polymers are either chemically or electrochemically deposited on the metal substrate^[64-71].

Mild steel is protected by an eco-friendly nanostructured conducting polymer/oil polyurethane composites, as shown in Figure 4^[72]. The camphor sulphonic acid (CSA) doped poly(1-naphthylamine) (PNA) dispersed in linseed oil polyurethane (LOPU) coatings were found to exhibit promising corrosion resistance performance.

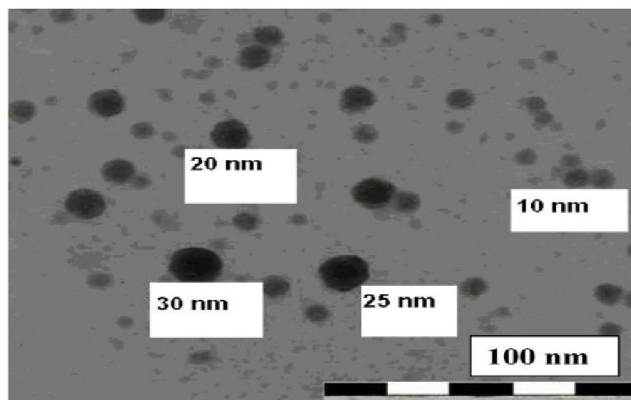


Figure 4 : TEM micrographs of nanostructured conducting polymer/oil polyurethane composites^[72].

Surface modification

The high-current pulsed electron beam (HCPEB) technique has been proven to be an efficient method for surface modification of alloys^[73,74]. Modifications improve the overall performance of alloys such as microhardness, corrosion resistance, and wear resistance. The structure and phase transformations in the

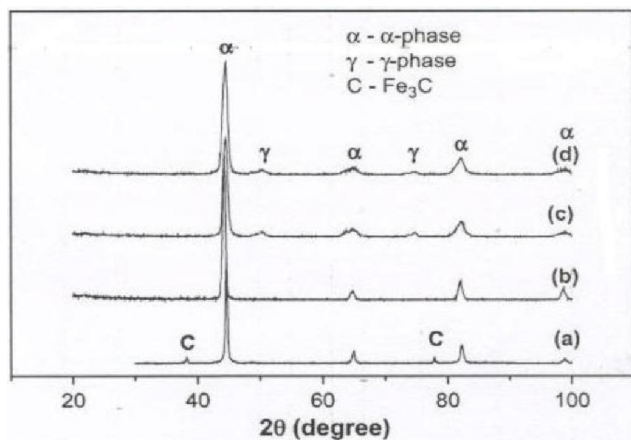


Figure 5 : XRD patterns collected from the surface of the initial no. 20 steel (a), irradiated with 1 pulse (b), 5 pulses (c), and 10 pulses (d). The energy density of HCPEM is 4 J cm^{-2} ^[73].

near-surface layers of a low carbon steel (0.2 wt.% C) subjected to a high-current pulsed electron beam (HCPEB) treatments have been investigated by using electron microscopy and X-ray diffraction (XRD)^[73]. A nanostructure consisting of cementite and C-saturated austenite is formed in the near-surface region after multiple bombardments. This is confirmed by the XRD patterns shown in Figure 5. According to the peak profile analysis, the average grain sizes of the γ phase (austenite) in the surface layer after the 5- and 10-pulse bombardments by the HCPEB are about 6.5 and 4.2 nm, respectively.

Stainless steel corrosion and nanostructure

The family of stainless steels (SS) is large and varied; in fact, there are more than 100 registered types. Each of these were originally designated for some specific use. For example, SS316 is used for severe environments. Of course, there are many industrial processes that require a higher level of resistance to corrosion. Carburizing has been applied to austenitic stainless steel to promote increased wear and corrosion resistance^[75]. Nanometric-sized carbide-based crystallites have been synthesized successfully through the pulsed nanocrystalline plasma electrolytic carburizing method on the surface of 316 austenitic stainless steel^[76]. It was found that the corrosion resistances of coated samples has a direct relationship with the average size of complex carbide-based nanocrystallites. The synthesized carbide-based crystallites exhibit average sizes at around 37–80 nm. Figure 6 shows the average sizes of nanocrystallites of different samples found through the process. The minimum average size of nanocrystals was found to be 37.7 nm in 600 V of peak of applied cathodic voltage, 10 kHz of frequency of pulsed current, 40 °C of temperature of electrolyte, 10 min of treatment time^[76].

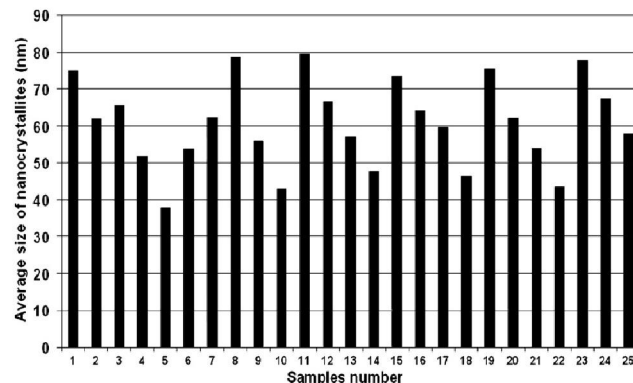


Figure 6 : Average size of nanocrystallites for different treated samples^[76].

Figure 7a and b shows the polarization resistances of different samples found through the potentiodynamic

corrosion tests performed after surface hardening treatment. The polarization resistances due to corrosion in specimen groups treated at different conditions varied between 153.4 k Ω /cm² and 635 k Ω /cm². The figure explains which specimen has maximum or minimum corrosion resistance. From the above results, it can easily be said that a high corrosion resistance has been obtained with higher applied voltages and treatment times of carburizing. These results indicate that the corrosion resistances of the obtained layers are a direct function of the average size of the nanocrystallites^[76].

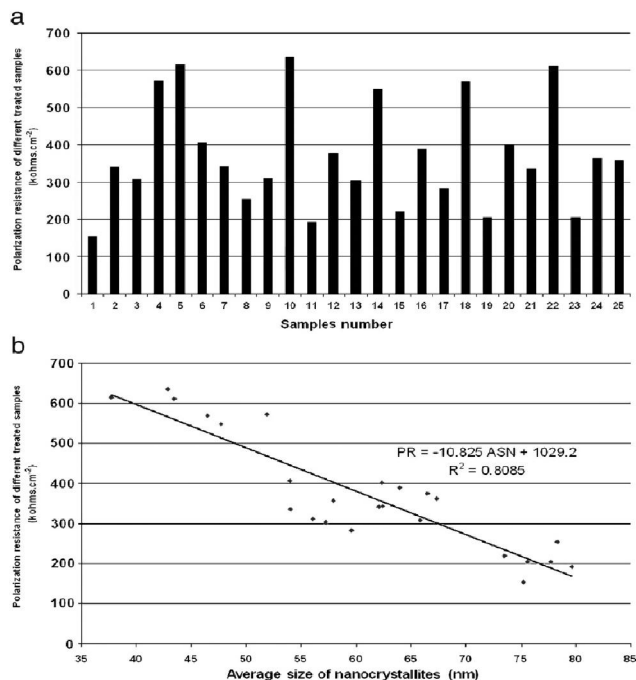


Figure 7: (a) Polarization resistances of different treated samples (b) vs. the average size of nanocrystallites^[76].

Improvement in the surface layers' properties by changing their structure remains actual due to the fact that the destruction of the materials, including fatigue failure, wear and corrosion depends usually on the surface structural state^[77]. The surface nanostructure, which is formed in the surface layers with thickness of about of 30–50 nm^[78-81], plays a main role in the enhancement of properties. At the same time, only a few recent studies have paid attention to the corrosion behavior of stainless steels with nanograined surface structure^[82-84]. These studies have shown that the corrosion resistance can also be markedly improved, particularly by shot peening^[85] or sandblasting with subsequent low-temperature annealing^[86,87]. For example, A nanocrystalline surface layer was produced on an AISI-321 stainless steel by severe plastic deformation via ultrasonic peening (UP)^[88,89]. The nanostructured surface layer formed after straining

already contains mainly the martensite nanograins characterized by an average size of about 10 nm. Grain size increased gradually up to 60 nm within the layer containing both austenite and martensite phases at a depth of about 30 nm from the treated surface. Both the microhardness behavior of the stainless steel surface and its corrosion performance in 3.5% NaCl solution can be enhanced by the UP. They are shown to be in correlation with: (i) the grain refinement process and (ii) the increase in the volume fraction of strain-induced martensite. Figure 8 shows potentiodynamic polarization curves obtained in 3.5% NaCl solution for as-annealed (curve 0) and as-peened samples. UP significantly improves the polarization behavior of the studied stainless steel, particularly within the processing duration range up to 3 min (curves 1–3).

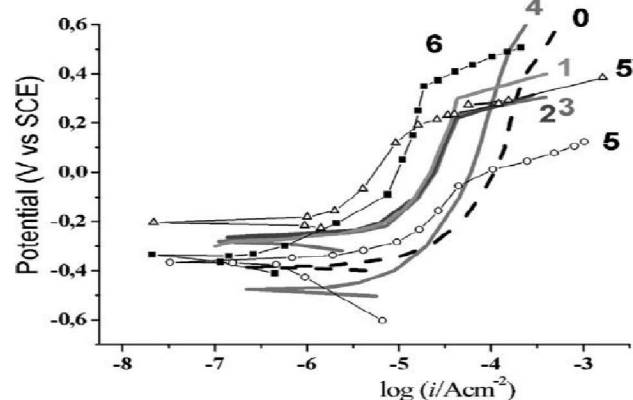


Figure 8 : Potentiodynamic polarization curves of as-annealed (dashed curve 0) and UP-processed samples (curves numbering corresponds to sample markings) of AISI-321 stainless steel obtained in 3.5% NaCl solution^[87]. Curves 5 and 5 (open circles and open triangles, respectively) are replotted from ref.^[86] for samples of AISI-304 stainless steel after sandblasting and sandblasting + annealing, respectively. Curve 6 (solid square) reflects data of ref.^[85] for sample of 1Cr18Ni9Ti stainless steel after shot peening.

Effect of nanostructure on passive film

Nanostructure changes the thickness of passive film. XPS Cr spectra from the passive films in 3.5% NaCl solution on nanostructure (NS) coating and the cast alloy are shown in Figure 9^[90]. After 40 s bombardment using the same bombardment parameters, the Cr³⁺ peak disappeared in the passive film on the NS coating but was still present in the film on the cast alloy. This indicates that the passive film on the NS coating was thinner than that on the cast alloy in normal NaCl solution. However, nanostructure increased the thickness of passive film on the magnesium alloy with rare earth elements^[90]. It is well known that the passive film on the magnesium alloy is mainly the corrosion product layer on the sample, which blocks the dissolution of the material and inhibits the corrosion.

Therefore, nanostructure promotes the dissolution of alloy and forms more products on the sample. Finally, the film layer was much thicker than that of the cast alloy. Nanostructure also changes the compact property of the passive film. After cathodic reduction, the variation of current with time could be measured at a fixed potential. If the contribution of the double layer charge is neglected, the initial drop of current density should be related to the growth of a protective film on the electrode surface. The current decreases with time as follows^[91]:

$$I = 10^{-A + k \log t} \quad (6)$$

where I represents current density, t is time, A is constant and k represents the slope of the double-log plot for potentiostatic polarization. $k = -1$ indicates the formation of a compact, highly protective passive film, while $k = -0.5$ indicates the presence of a porous film, growing as a result of a dissolution and precipitation process. It is found that a porous passive film was present on the 309 stainless steel and nanostructure

improved formation of a compact film^[92], which is an interesting phenomenon.

Corrosion resistance of aluminum alloy

Aluminum alloys have a wide diversity of industrial applications because of their high specific strength, lightweight and corrosion resistance. Therefore these alloys motivate considerable interest to the transportation and aviation industries^[93-96]. In some applications at room and elevated temperatures it is observed that these alloys show weak mechanical properties such as low wear resistance. So, in order to enhance the mechanical specifications of these materials, development of bulk aluminum based composites and coatings have been the subject of great interest^[97,98]. Recently, in another approach, formation of nanostructured aluminum alloys has received a great attention. Production of the nanostructured alloys has been performed by novel techniques such as mechanical alloying^[99]. Non-equilibrium nature of this process makes fabrication of homogenous supersaturated solid solutions starting from blended elemental powders possible^[100,101]. Nanostructured Al7075 was synthesized by mechanical alloying. The produced structure was isothermally heat-treated at 125–500 °C for 1–3 h under argon atmosphere. The results showed that after 15 h of milling, an Al–Zn–Mg–Cu supersaturated solid solution with a grain size of 35nm was obtained. The XRD patterns of the milled powders (Al–5.6 wt% Zn–2.5 wt% Mg–1.6 wt% Cu) for different milling times were recorded. In the early stages of milling, only broadening of the Al, Zn, Mg and Cu peaks accompanied by remarkable decrease in their intensities occurred as a result of refinement of crystalline size and enhancement of lattice strain. Increasing milling time to 15 h, led to the disappearance of Zn, Mg and Cu peaks, while Al (1 1 1) peak shifted to higher angles (Figure 10).

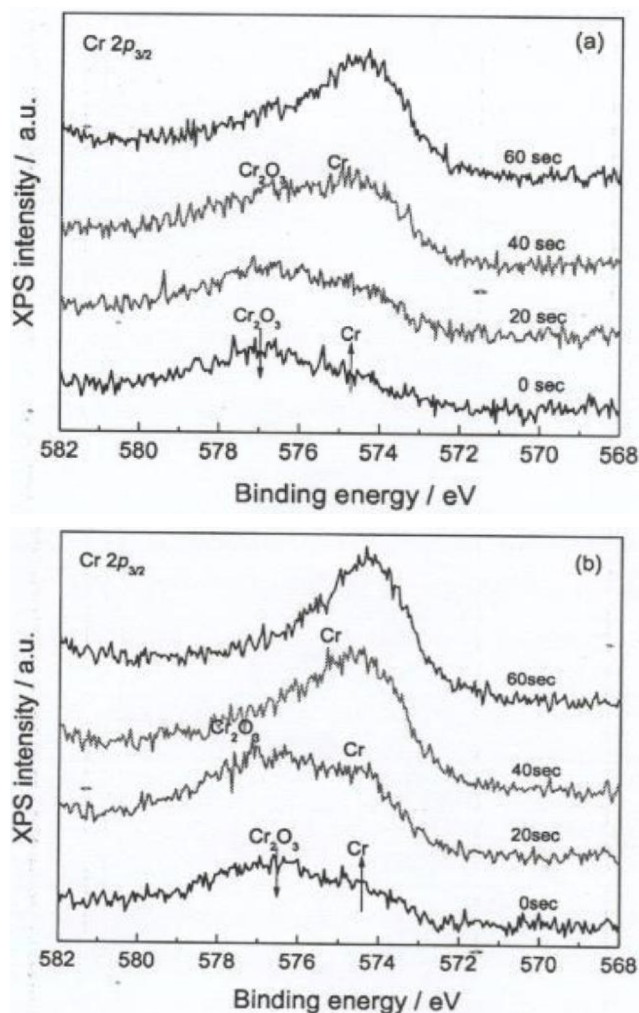


Figure 9 : Cr 2p XPS depth profile spectra from the cast alloy (a) and the NC coating (b) after passivation 30 min at 0 V in 3.5% NaCl solution. The depth is indicated in spectrum^[87]

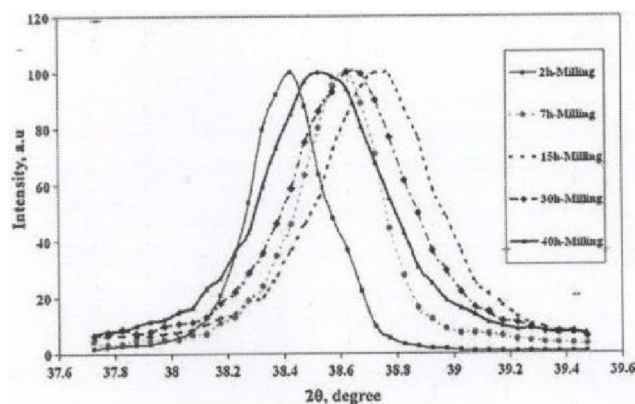


Figure 10 : Displacement of Al (1 1 1) XRD peak after 2, 7, 16, 30, 40 h milling^[99].

Localised corrosion of aluminum (Al) alloys is a significant problem worldwide, particularly for the aerospace and transportation sectors. Nominally, improvements in the mechanical performance of Al-alloys result from the development of heterogeneous microstructures, due to specific, often complex, alloying regimes^[102]. There is a microgalvanic relationships are able to hold into the nanoscale via observation of localized corrosion on a precipitate in an Al-alloy that was on the order of 10nm in size. The small grain size improves the elemental diffusion, which changes the composition of the protective film, forms more compact film and influences the morphology and growth process of passive film. The small grain size also changes the surface condition, which influences the ions adsorption. ions incorporating into the passive film influences the semiconductor property. All of them increase the corrosion resistance of materials.

CONCLUSION

Nanostructured materials are important due to their unique properties that may lead to new and exciting applications. Properties of nano-structured electrodeposits such as hardness, wear resistance and electrical resistivity are strongly grain size (1-100 nm) dependent. Nanocrystallization decreases the grain size and changes the surface condition, which significantly influences the electrochemical corrosion behaviors of metals/alloys in liquid system. A variety of advanced techniques have been developed to attain the nanostructure. Significant progress has been made in various aspects of synthesis of nano-scale materials. There are many applications of the nanomaterials, which are made to improve the devices and industries. The application of nanotechnology in the field of corrosion prevention of metals is very important. Formation of nanostructured was processed by different techniques. Nanometric-sized carbide-based crystallites have been synthesized successfully through the pulsed nanocrystalline plasma electrolytic carburizing method on the surface of 316 austenitic stainless steel. It was found that the corrosion resistances of coated samples has a direct relationship with the average size of complex carbide-based nanocrystallites. A high corrosion resistance has been obtained with higher applied voltages and treatment times of carburizing. These results indicate that the corrosion resistances of the obtained layers are a direct function of the average size of the nanocrystallites. In local corrosion, nanocrystallization increases the unstable points on the surface of the materials, which increases the possibility of local corrosion.

However, the excellent ability of element diffusion helps to heal the local corrosion points, which inhibits the growth of the local corrosion.

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